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EXPERIMENTAL STUDY OF THE EFFECT OF COLUMN LENGTH AND PRESSURE ON THE HETP IN GAS CHROMATOGRAPHY

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SUMMARY

HETP *vs.* carrier gas velocity curves were measured on columns of different lengths operated under laminar flow conditions at either a constant outlet or a constant inlet column pressure, as well as on columns of a given length operated at various levels of the outlet or the inlet column pressure, respectively. Both high and low amounts of liquid stationary phase on the support were employed. With columns operated at a constant outlet pressure, the minima on the curves were shifted towards lower HETP and flow velocity values and the ascending branches of the curves acquired a more dished curvature upon increase of column length. The reverse situation was encountered with columns operated at a constant inlet pressure. An increase in the mean absolute column pressure brought about by an increase of either the outlet or the inlet column pressure always resulted in a pronounced decrease of the minimum HETP and optimum velocity, as well as in a steeper and straighter ascending branch of the HETP *vs.* velocity curve when working with the high liquid load packing; with a low loading of liquid stationary phase an inappreciable decrease of the minimum HETP occurred under the above conditions. Disagreements between the present results and those obtained by other authors are discussed.

In a previous paper[1], the effects of varying the parameters determining the absolute column pressure on the HETP in gas chromatography have been discussed. It was shown that the above effects may be described by the equations

$$\bar{H} = A + \frac{B_s}{\bar{u}} + \frac{B_m}{\bar{u}P_o + (\eta L/2K)\bar{u}^2} + C_m P_o \bar{u} + C_m(\eta L/2K)\bar{u}^2 + C_s\bar{u} \qquad (1)$$

and

$$\bar{H} = A + \frac{B_s}{\bar{u}} + \frac{B_m}{\bar{u}P_i - (\eta L/2K)\bar{u}^2} + C_m P_i \bar{u} - C_m(\eta L/2K)\bar{u}^2 + C_s\bar{u} \qquad (2)$$

for columns operated under laminar flow conditions and at moderate pressures and pressure drops. Eqns. 1 and 2 refer to the cases of work at either a constant column outlet pressure (P_o) or a constant column inlet pressure (P_i); A, B_s, B_m, C_m, and C_s are the constants of the extended Van Deemter equation, L and K are the column length and the column permeability constant, η is the carrier gas viscosity coefficient, and $\bar{H}$ and $\bar{u}$ stand for the apparent HETP and the average carrier gas forward velocity determined from the column length and the gas hold-up time, respectively. The present work is an experimental version of the investigation to the above problems.

EXPERIMENTAL

The experiments were designed in such a way that they covered all the aspects indicated by eqns. 1 and 2. Packings with both a high and a low loading of liquid phase were used in columns of different lengths, operated at a constant outlet pressure and variable inlet pressure and *vice versa*, as well as in columns of a given length, operated at different constant levels of either the column outlet pressure or column inlet pressure, respectively.

The column lengths were 0.75 and 3 m, the longer one being made up of four 0.75 m segments. The column segments were stainless steel tubes of 3 and 5 mm inner and outer diameters, respectively, filled, in the straight state, by pouring the packing in while gently tapping the tube for about 2 h and making sure that the weights of packing in the individual segments did not vary more than 0.05 g. The spaces, necessary for plugging the packing, did not exceed 20 μl at each end of the segment; sleeve couplings with teflon sealings, providing for a leakproof face-to-face connection, were used. 25 and 3 wt.% dinonyl phthalate on Chromosorb P 60/80 mesh were employed as the column packings. They were prepared by the slurry technique using dichloromethane as the solvent. The support (Carlo Erba, Italy) had previously been dried at 200° for 3 h prior to coating it with the liquid phase (Griffin & George Ltd., Great Britain). The weights per 0.75 m segment of the 25 and 3% packings were 3.43 and 2.70 g, respectively. Pentane and hexane were used as the solutes with the high and the low load of liquid phases, respectively, the column temperature being kept at 40° in all cases.

The measurements were carried out on a Becker Multigraph 409 (Becker Delft, Holland) equipped with a Servogor RE 512 recorder (Goerz Electro G.m.b.H., Austria); thermal conductivity detection was used and hydrogen was the carrier gas. The injection port and detector temperatures were maintained at the column temperature (40°). The built-in gas flow control unit was disconnected and substituted by an external one in order to be able to extend the inlet pressure range beyond the conventional limits. Further, the measuring cell outlet was connected to a unit comprising a pressure gauge, damping bottle, and needle valve, thus providing control for the column outlet pressure. The flow diagram of the whole pneumatic arrangement is shown in Fig. 1. The use of the narrow-bore sample port insert liner, supplied with the apparatus, as well as the small dead volume of the path between the column outlet and the detector measuring cell are supposed to result in minimum zone broadening effects outside the column.

The sample itself consisted of the saturated vapours of either pentane or hexane at 25° in hydrogen containing traces of air. About 40 μl charges of this sample were injected by a Zimmermann syringe (Zimmermann, Leipzig). This method of sample

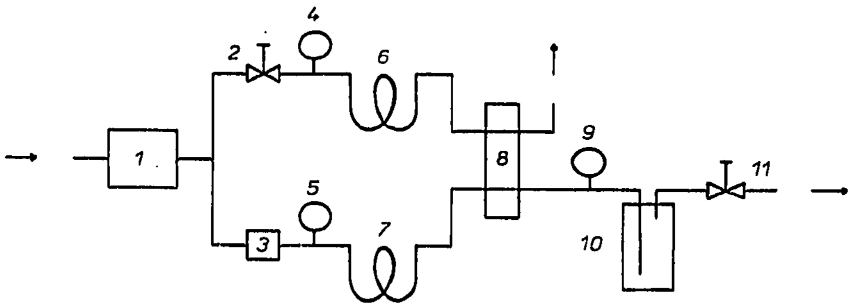

Fig. 1. Flow diagram of the pneumatic arrangement of the gas chromatograph used. 1 = tank cylinder pressure controller; 2 and 11 = needle valves; 3 = Brooks flow controller; 4, 5 and 9 = pressure gauges; 6 = reference column; 7 = measuring column; 8 = measuring cell; 10 = damping bottle.

introduction resulted in optimal sizes of both the pentane (hexane) and air peaks while preventing the possible broadening effects incidental to the volatilization of a liquid sample charge. Full detector sensitivity was employed at bridge currents varying between 250–300 mA.

The mean carrier gas velocity was determined by means of the air peak maximum. The $\bar{H}$ values were calculated from the formula $\bar{H} = L/8(\ln 2)(b/\Delta b_{1/2})^2$ where b and $\Delta b_{1/2}$ designate the peak maximum distance from the start line and the peak width at the half peak height, respectively[2].

The laminar flow of the carrier gas was controlled by checking the linearity of the dependence of the directly measured carrier gas volume flow rate, at the given column outlet pressure, on the parameter $(P_i^2 - P_o^2)/P_o$.

RESULTS AND DISCUSSION

The curves in Fig. 2 refer to measurements with the high loading of liquid phase on the support and a constant column outlet pressure. Curves 1 and 2 were obtained with the 3 and 0.75 m long columns, respectively, the column outlet being kept at the atmospheric pressure in both cases. Curve 3 was obtained with the 0.75 m column and an outlet pressure of 3 atm. The shift of the minimum towards lower $\bar{u}$ and $\bar{H}$ values upon elongating the column is perceptible but not very significant; this is due to the fact that the minimum occurs in a region of relatively low flow velocities and, accordingly, low flow-induced excess pressures with high liquid phase loads, *i.e.*, the ratio of the mean absolute column pressures corresponding to the minima on the curves for the longer and the shorter column, respectively, approaches unity.

On the other hand, with the ascending parts of the above curves, in the region of the highest flow velocities employed, the slope of the tangent to curve 1 (longer column) is about twice as large as that to curve 2 (shorter column). This is obviously due to the considerably greater curvature of the branch concerned of curve 1. In the above flow velocity region, the ratio of the slopes of the tangents to curves 1 and 2 should obey the expression[1] $\{C_s + C_m[(\eta L_1\bar{u}/K) + P_o]\}/\{C_s + C_m[(\eta L_2\bar{u}/K) + P_o]\}$, where L_1 and L_2 stand for the lengths of the longer and the shorter column, respectively.

Comparison of curves 3 and 2 shows that the effects of the increase of the column outlet pressure, while maintaining constant column length are similar to the above

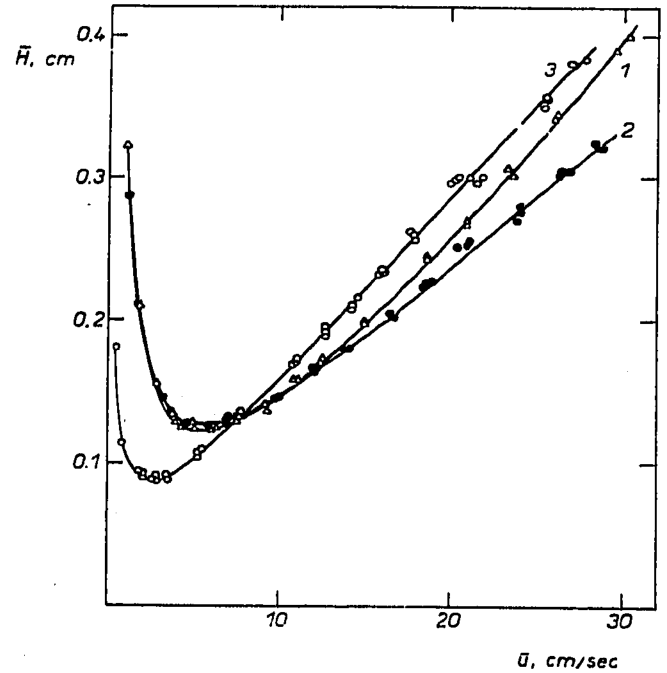

Fig. 2. Measurements at a constant column outlet pressure, high loading of liquid phase on the support. 1 = L 3 m, P_o 1 atm., P_i 1.1–3.91 atm; 2 = L 0.75 m, P_o 1 atm, P_i 1.02–1.67 atm; 3 = L 0.75 m, P_o 3 atm, P_i 3.06–3.75 atm.

column length effects in so far as the trends in the changes of the shape and location of the curve are concerned. The shift of the minimum upon the increase in the column outlet pressure is much more significant than that caused by the increase in the column length. This state of affairs reported earlier by SCOTT[3], is obviously brought about by the fact that the mean absolute column pressure corresponding to the minimum on curve 3 is much higher than that incidental to the minima on both curve 2 and even curve 1; owing to low flow velocities corresponding to the minima on all the curves in Fig. 2, an increase in the column outlet pressure is more effective than an increase in the column length in shifting the minimum towards the region of lower $\bar{u}$ and $\bar{H}$ values.

As for the effect of the outlet pressure on the ascending branch of the $\bar{H}$ *vs.* $\bar{u}$ curve, the ratio of the slopes of the tangents to curves 3 and 2, in the region of high velocities, should be given by $\{C_s + C_m[(\eta L_2\bar{u}/K) + P_{o3}]\}/\{C_s + C_m[(\eta L_2\bar{u}/K) + P_{o2}]\}$ where P_{o3} and P_{o2} are the higher and the lower column outlet pressure, respectively, which is in conformity with the courses of the respective curves in Fig. 2.

Another typical effect incidental to the increase in the column outlet pressure is the straightening of the ascending branch of the curve (*cf.* curve 3). This effect may be explained by referring to the relation for the respective slopes, $d\bar{H}/d\bar{u} = C_s + C_m[(\eta L\bar{u}/K) + P_o]$. It is apparent from this relation that the significance of the $\bar{u}$-containing term, which is responsible for the dished curvature of the ascending branch, decreases with increasing values of P_o. On the whole, the situation depicted in Fig. 2 is in agreement with eqn. 1.

It is worth mentioning that the results of our measurements are at variance with the results obtained by HALÁSZ *et al.*[4] for a similar system. The above authors found quite opposite trends in the changes of the slope of the ascending branch of the curves and the position of the minimum upon increasing the column outlet pressure. On the other hand, our results are in agreement with those found by LOCKE AND BRANDT[5]. It is interesting to notice that HALÁSZ *et al.*'s measurements were carried out at absolute column pressures varying within fairly wide limits (column outlet pressures of within 0.5–6.0 atm) with N_2 carrier gas, whereas LOCKE AND BRANDT performed their measurements at subatmospheric column outlet pressures using He and CO_2 as carrier gases, which implies substantially lower absolute column pressures in LOCKE AND BRANDT's case. Our measurements were carried out at absolute column pressures comparable with those employed by HALÁSZ *et al.*, but with H_2 as the carrier gas, so that the carrier gas density approached more or less that in LOCKE AND BRANDT's measurements. Hence, it seems that it is the carrier gas density that decides whether the effects of the mean absolute column pressure on the $\bar{H}$ *vs.* $\bar{u}$ curve are predictable, in virtue of the simple mean pressure and stream-line flow concepts[1]. The above situation indicates the contingency of pressure induced turbulence occurring in the column.

Fig. 3 illustrates the situation in the case of measurements with the high loading of liquid phase on the support and a constant column inlet pressure. Again, the shifts in the slope and location of the curves upon changing either the column length or the column inlet pressure are in good agreement with eqn. 2. Curves 1 and 2 were obtained by measurements with the longer and the shorter column, respectively, at a column inlet pressure of 5.5 atm. Curve 3 was obtained with the shorter column at a column inlet pressure of 3.0 atm. The gentler slope of the ascending branch and the higher minimum HETP with curve 1, as compared to curve 2, is caused by the necessity of

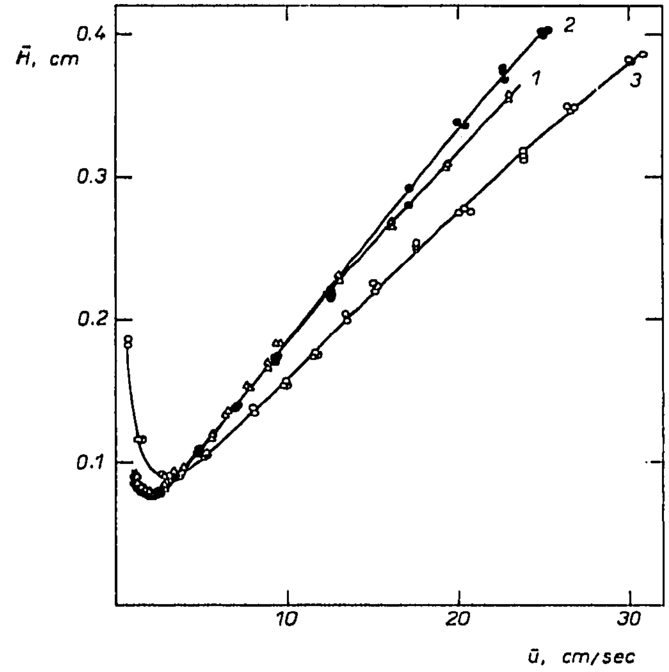

Fig. 3. Measurements at a constant column inlet pressure, high loading of liquid phase on the support. 1 = L 3 m, P_i 5.5 atm, P_o 5.4–3.52 atm; 2 = L 0.75 m, P_i 5.5 atm, P_o 5.48–4.83 atm; 3 = L 0.75 m, P_i 3.0 atm, P_o 2.92–2.16 atm.

having to apply a lower column outlet pressure with the longer column to get a given flow velocity than in the case of the shorter column. This obviously implies a lower mean absolute column pressure in the longer column than in the shorter one for the given flow velocity; the ratio of the slopes of the tangents to curves 1 and 2 should correspond to: $\{C_s + C_m[P_t - (\eta L_1\bar{u}/K)]\}/\{C_s + C_m[P_t - (\eta L_2\bar{u}/K)]\}$ in a region of high flow velocities. Variations in the column inlet pressure parameter have the same consequences here as in the work with constant column outlet pressures. The decrease of the mean absolute column pressure by decreasing the column inlet pressure from 5.5 to 3.0 atm (curve 3) results in a pronounced rise of the minimum HETP and in a gentler slope of the ascending branch of the curve; the ratio of the slopes of curves 3 and 2 is characterised by $\{C_s + C_m[P_{t3} - (\eta L_2\bar{u}/K)\}/\{C_s + C_m[P_{t2} - (\eta L_2\bar{u}/K)]\}$. All curves in Fig. 3 display perceptibly domed ascending branches, the curvature again being most notable in the case of the lowest mean absolute column pressure (curve 3). The domed curvature is due to the negative sign of the factor $\eta L\bar{u}/K$ in the relation $\mathrm{d}\bar{H}/\mathrm{d}\bar{u} = C_s + C_m[P_t - (\eta L\bar{u}/K)]$, applicable at higher flow velocities.

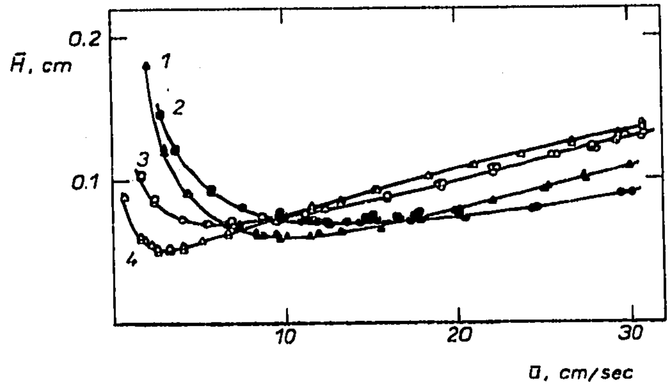

Fig. 4. Measurements with low loading of liquid phase on the support, 1,2,3 = constant column outlet pressure, 4 = constant column inlet pressure. 1 = L 3 m, P_o 1 atm, P_i 1.24–4.5 atm; 2 = L 0.75 m, P_o 1 atm, P_i 1.08–1.91 atm; 3 = L 0.75 m, P_o 3 atm, P_i 3.02–3.94 atm; 4 = L 3 m, P_i 6.5 atm, P_o 6.45–3.18 atm.

Fig. 4 illustrates the situation in the case of the low loading of liquid phase. Curves 1 and 2 correspond to measurements with an atmospheric column outlet pressure with the longer and the shorter column, respectively. Curve 3 represents the case of the shorter column operated at an outlet pressure of 3 atm. Curve 4 was obtained with the longer column operated at a constant inlet pressure of 6.5 atm. It is apparent from the comparison of curves 1 and 2 that the shifts of the minima towards lower flow velocities upon elongating the column are much more significant than in the corresponding case with a high concentration of liquid phase. However, the ratio of the slopes of the tangents to the curves at high velocities is similar to that for the corresponding curves obtained with the high concentrations of liquid phase, though the absolute values of the slopes are much lower with the lower concentration of liquid phase. This confirms the concept that the enhancement of the steepness of the ascending branch upon elongating the column or raising the column outlet pressure is, in practice, associated only with the situation in the gaseous phase and, consequently, that the absolute change in the slope is only slightly dependent on the stationary liquid loading.

The decrease of the minimum HETP with the increase of the column length is larger than that expected in terms of eqn. 1. This is very likely due to longitudinal diffusion within extracolumn spaces; the significance of the latter rises on decreasing the column length and the retentive capacity of the packing. The above extracolumn contribution to the HETP, $\bar{H}_e$, can be derived from the expression $\bar{H}_e = 2RDV_e/Lv$ where R is the retardation factor, D is the diffusion coefficient of the solute in the mobile phase, V_e is the extracolumn volume, v is the mobile phase volume flow-velocity within the volume V_e, and L is the column length. This explanation is supported by the fact that an increase in the column outlet pressure with the same column (*cf.* curve 3) resulted in practically no change in the minimum HETP. The slight drop in the minimum HETP with curve 4, compared to curve 1, may be regarded as incidental to the appreciably higher mean absolute column pressure corresponding to the minimum on curve 4.

CONCLUSIONS

Under laminar carrier gas flow conditions and at moderate pressures and pressure drops, the variations in the course of the HETP *vs.* flow velocity curves, brought about by varying the column length and by changing the parameters of either the column outlet or inlet pressures, are in good agreement with the respective variations predictable by virtue of simple concepts of the role of the mean absolute column pressure, for both high and low concentrations of liquid phase on the support.

Under the above conditions, column elongation results in a slightly lower or unchanged minimum HETP, lower optimum carrier gas flow velocity, and a slight increase in the dished curvature of the ascending branch of the $\bar{H}$ *vs.* $\bar{u}$ curve when working at a constant column outlet pressure. In the case of constant column inlet pressure, an increase in the column length leads to a higher or unchanged minimum HETP, higher optimum flow velocity, and enhanced domed curvature of the ascending branch of the curve.

In both the above-mentioned cases, an increase of the mean absolute column pressure by elevating either the outlet or the inlet column pressure results in a remarkable shift of the minimum on the $\bar{H}$ *vs.* $\bar{u}$ curve towards lower values of both $\bar{H}$ and $\bar{u}$ when working with high concentrations of liquid phase and to little or no decrease in the minimum $\bar{H}$ and a significant decrease of the optimum $\bar{u}$ in case of low loads of liquid phase. The ascending branch of the $\bar{H}$ *vs.* $\bar{u}$ curve grows steeper and straighter upon elevating the absolute column pressure at a constant column length.

The conflicting situations arrived at by other authors seem to stem partly from pressure induced turbulent flow of the carrier gas in the column.

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